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ORIGINAL PAPER

Synthesis and Characterization of Molecules Containing Thiazole and Oxazole Moieties and Study of ESIPT Phenomenon

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Abstract Two novel ESIPT molecules, 2-[4-(1,3-benzothiazol-2-yl)naphtho[1,2-*d*][1,3]oxazol-2-yl]phenol **9a** and 4-[4-(1,3-benzothiazol-2-yl)naphtho[1,2-*d*][1,3]oxazol-2-yl]benzene-1,3-diol **9b** were synthesized by condensing 1-amino-3-(1,3-benzothiazol-2-yl)naphthalen-2-ol with 2-hydroxybenzoic acid and 2,4-dihydroxybenzoic acid respectively. The novel compounds were characterized by FT-IR, ^{1}H NMR, Mass spectral and elemental analysis. Effect of polarity on photo physical properties, absorption and emission were studied. Compounds showed single absorption and dual emission due to ESIPT phenomenon. The structural changes due to ESIPT phenomenon in terms of bond angle, bond distances and geometry were investigated by using Gaussian 03 software. These two novel ESIPT molecules are thermally stable up to 200 °C.

Keywords Thiazole · Oxazole · ESIPT · Fluorescence · Solvatochromism · DFT

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Introduction

Fluorescent molecules find extensive applications in the investigation of proteins in biological systems [1]. Dual emission spectroscopy is a strong tool to detect a protein binding site as well as H-bond donating and accepting ability. The use of a dual emitter gives a ratio metric response independent of the concentration of probe molecules [2].

Excited State Intramolecular Proton Transfer (ESIPT) molecules form a very effective basis for the design of probes with dual fluorescence. In this process, on UV excitation two isomers (enol E* and keto K*) are formed which are having different photo physical properties. These tautomeric forms immediately come at ground state with loss of energy in the form of fluorescence. This results into highly separated two emission bands [3–5]. Therefore ESIPT molecules show single excitation with dual emissions.

Amongst the large range of systems undergoing excited-state intramolecular proton transfer (ESIPT), compounds of the azole type, that is oxazole and thiazole, form an important class [6–13]. There are many reports describing the dependence of fluorescence on solvent polarity [14–17] as well as theoretical calculations regarding the geometry of the different conformers [18–23]. The azoles exhibit dual emission in polar solvents [24, 25].

One of the most important features of ESIPT molecules is the phenolic group, which participates in intramolecular hydrogen bonding with nitrogen. There are radical changes in the molecule around acidic and basic centers upon UV excitation. These changes generally lead to proton transfer from hydroxyl (enol) to nitrogen, generating the keto form of the carbonyl group in the process [22]. It has been shown

that different species coexist in the ground state [26] and the closed enol conformer alone is responsible for larger Stokes shift after undergoing ESIPT [27]. Most of the o-hydroxy azole type molecules undergoing ESIPT show larger Stokes shifts [28–32]. In continuation of our work in ESIPT molecules [33, 34], we report here two novel ESIPT molecules, their photo physical properties and DFT calculations.

This paper describes organic molecules containing both thiazole as well as oxazole units. The molecules **9a** and **9b** are synthesized by a synthetic sequence outlined in the synthetic scheme (Fig. 1) [35–37]. The target molecules **(9a and 9b)** are hitherto unknown and they are fully characterized by spectral techniques. These molecules show three emissions in highly polar aprotic solvent like DMF. Thermal stabilities and solvatochromism of these molecules are also reported. All these molecules undergo ESIPT phenomenon having larger Stokes shifts.

Experimental

Materials

3-Hydroxynaphthalene-2-carboxylic acid (BON acid), 2-aminothiophenol, 4-aminobenzenesulfonic acid, 2-hydroxybenzoic acid, 2,4-dihydroxybenzoic acid, phosphorus trichloride, sodium nitrite, sodium dithionite, toluene, xylene, ethyl acetate and methanol were purchased from S.D. Fine Pvt. Ltd. Mumbai. Solid reagents were characterized by melting point and used without purification. Liquid reagents were distilled at their boiling points and used immediately. All solvents were used after necessary purification and drying according to standard processes.

Synthesis

Synthesis of 3-(1,3-Benzothiazol-2-yl)Naphthalen-2-ol **3** *[35]*

Phosphorus trichloride (2.6 mL, 4.13 g, d=1.57 gL^{-1}, 0.03 mol) was added drop wise to a solution of the 3-hydroxynaphthalene-2-carboxylic acid (BON acid) (6.2 g 0.033 mol) and 2-aminothiophenol (3.85 mL, 4.5 g, d= 1.17 gL^{-1}, 0.036 mol) in toluene (50 mL), maintaining the temperature below 40–45 °C. The mixture was boiled vigorously under reflux for 4 h, whereupon the cooled solution was made alkaline with aqueous sodium carbonate solution (20 %w/v). Toluene was removed by vacuum distillation and the solid remained was collected and purified by recrystallization from methanol.

Yield: 82 %; M.p. 182–184 °C (lit. 183 °C) [35].

Preparation of 4-{(E)-[3-(1,3-Benzothiazol-2-yl)-2-Hydroxynaphthalen-1-yl]Diazenyl}Benzenesulfonic Acid **6** *[36]*

A mixture of sulfanilic acid (10.5 g, 0.055 mol) and sodium carbonate (2.65 g, 0.025 mol) in water (100 mL) was heated until a clear solution obtained. The reaction mixture was then cooled to about 15 °C. A cold solution of sodium nitrite (3.8 g, 0.055 mol) in water (10 mL) was added to the above mixture. The resulting solution was slowly poured over 35 % hydrochloric acid (14.2 mL, 14.9 g, d=1.2 gL^{-1}, 0.165 mol) at 0–5 °C, with constant stirring. The progress of the reaction was checked with starch- iodide paper.

3-(1,3-Benzothiazol-2-yl)naphthalen-2-ol (0.01 mol, 2.77 g) was dissolved in a mixture of 80 % methanol in water (50 mL) containing sodium hydroxide (0.4 g, 0.01 mol). A clear yellow solution was obtained. The reaction mixture was then cooled to 5 °C. The above diazotized amine **5** was slowly added with constant stirring and maintaining temperature at 5 °C and pH between 9 and 10. The acid dye **6** was formed and recrystallized from methanol.

Yield: 80 %; M.p. > 300 °C.

Anal. Calcd. for $C_{23}H_{15}N_3O_4S_2$ (461.52 $gmol^{-1}$): C, 59.86; H, 3.28; N, 9.10; S, 13.90.

Found: C, 59.79; H, 3.21; N, 9.09; S, 13.80.

FT-IR (KBr, cm^{-1}): 3460, 1606, 3040, 1552, 1193.

^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 2.15 (s, 1H, SO_3H); 4.62 (s, 1H, OH; D_2O exchangeable) 7.76–8.92 (m, 13H, Ph).

m/z: 462(M+1).

Preparation of 1-Amino-3-(1,3-Benzothiazol-2-yl)Naphthalen-2-ol 7 [37]

Sodium dithionite (19.4 g, 0.11 mol) was added to the above suspension of dye at pH 8-9. The reaction mixture was heated to 50 °C and the alkaline pH was maintained throughout the reaction. After complete discharge of dye color, compound **7** separated out, and was filtered and recrystallized from ethyl acetate.

Yield: 90 %; M.p. 162–164 °C.

Anal. Calcd. for $C_{17}H_{12}N_2OS$ (292.36 $gmol^{-1}$): C, 69.86; H, 4.14; N, 9.58; S, 10.97.

Found: C, 69.56; H, 4.04; N, 9.51; S, 10.79.

FT-IR (KBr, cm^{-1}): 3423, 3319, 3051, 1643, 1494, 1456.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.54 (s, 2H, NH_2), 7.46–8.25 (m, 9H, Ph), 12.28 (s, 1H, OH).

m/z: 293(M+1).

Synthesis of **9a** *and* **9b**

Phosphorus trichloride (2.6 mL, 4.13 g, d=1.57 gL^{-1}, 0.03 mol) was added drop wise to a solution of the hydroxybenzoic acid **8a** or **8b** (0.033 mol) and 1-amino-3-(1,3-

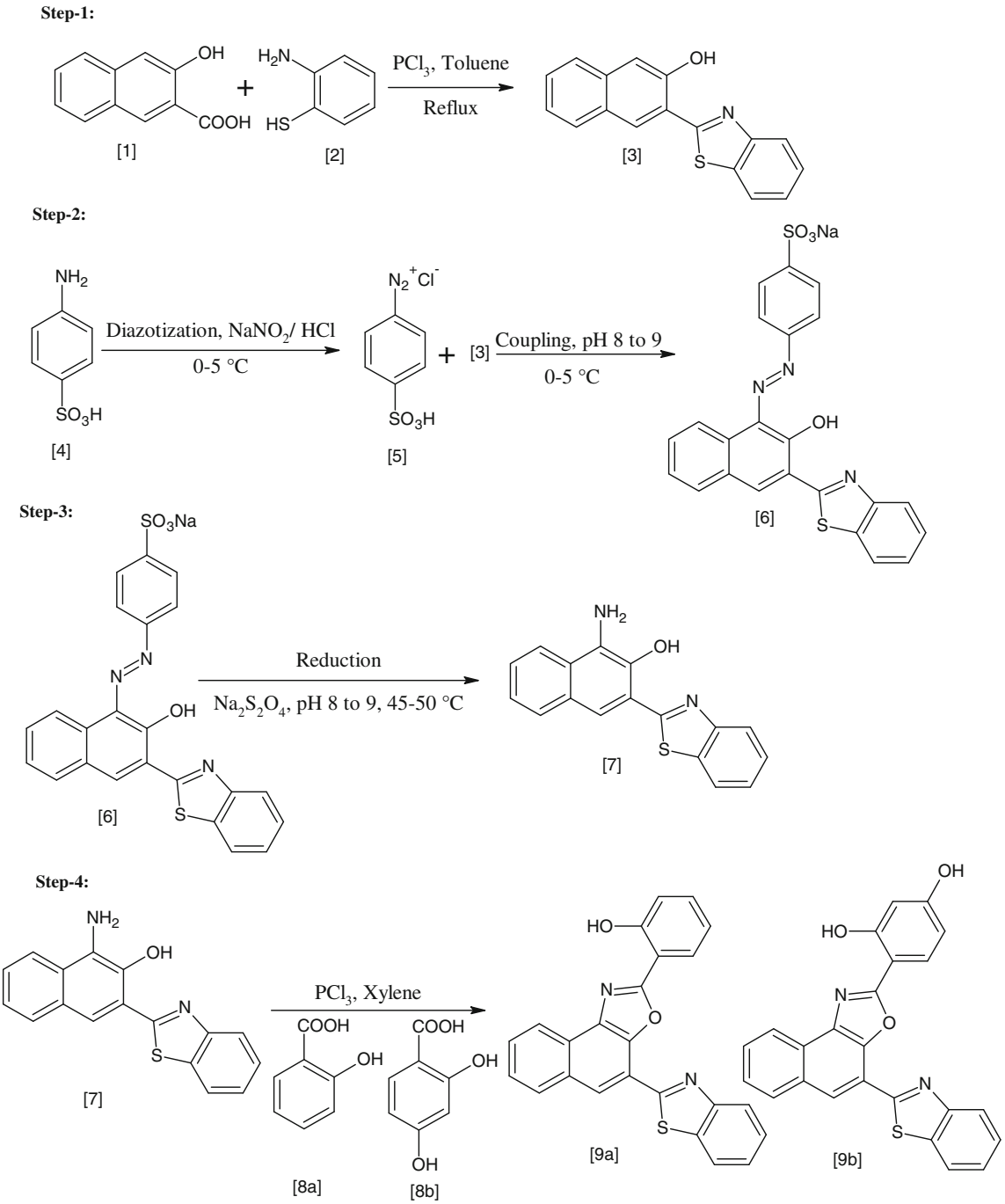

Fig. 1 Synthesis of ESIPT benzothiazolyl naphthooxazol phenol derivatives

benzothiazol-2-yl)naphthalen-2-ol **7** (10.51 g, 0.036 mol) in xylene (50 mL), maintaining the temperature at 40–45 °C. The mixture was then refluxed for 5 h and allowed to cool to room temperature and made alkaline with 20 % aqueous sodium carbonate solution. The reaction mixture was then filtered and compounds **9a** and **9b** were recrystallized from methanol.

2-[4-(1,3-benzothiazol-2-yl)naphtho[1,2-d][1,3]oxazol-2-yl]phenol **9a** Yield: 72 %; M.p. 140–142 °C.

Anal. calcd. for $C_{24}H_{14}N_2O_2S$ (394.45 $gmol^{-1}$) C, 73.09; H, 3.58; N, 7.10; S, 8.13.

Found: C, 72.86; H, 3.48; N, 1.02; S, 8.08.

FT-IR (KBr, cm^{-1}): 3410, 3053, 1653, 1573, 1521.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.88 (s, 1H, OH, D_2O exchangeable), 7.38–8.02 (m, 13H, Ph), 12.12 (s, 1H, OH, hydrogen bonding).

m/z: 395 (M+1).

4-[4-(1,3-benzothiazol-2-yl)naphtho[1,2-d][1,3]oxazol-2-yl]benzene-1,3-diol ***9b*** Yield: 69 %; M.p. 170–172 °C.

Anal. calcd. for $C_{24}H_{14}N_2O_3S$ (410.45 $gmol^{-1}$) C, 70.23; H, 3.44; N, 6.83; S, 7.81.

Found: C, 70.15; H, 3.39; N, 6.79; S, 7.79.

FT-IR(KBr, cm^{-1}): 3414, 3049, 1613, 1579, 1527.

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 3.40 (s, 2 H, OH, D_2O exchangeable), 7.56–8.88 (m, 12 H, Ph), 11.56 (s, 1H, OH, hydrogen bonding).

m/z: 411.5 (M+1).

Characterization

All melting points were recorded by open capillary on Sunder Industrial Product and are uncorrected. All reactions were monitored by using precoated silica gel aluminum backed plates, Kisel gel 60 F_{254} Merck (Germany). UV- Visible absorption measurements were carried out using a Spectronic Genesys 2 spectrophotometer with 1 cm quartz cells. The excitation wavelength was taken as λ_{max} of compound. The scan range was 250 to 650 nm. Fluorescence emission measurements were recorded on Cary Eclipse fluorescence spectrophotometer (Varian, Australia) using 1 cm quartz cells. Quantum yield of these compounds were calculated using Anthracene and Fluorescein as standards. FT-IR analysis was performed on a FTIR-8400 S SHIMADZU spectrophotometer. Thermo gravimetric analysis was carried out on a SDT Q600 TA Instruments and elemental analysis was carried out on a Harieus rapid analyzer. Method for thermo gravimetric analysis: Ramp 10 °C per minute from ambient temperature to 600 °C under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on VXR 400-MHz instrument using TMS as an internal standard and $CDCl_3$, CD_3OD or DMSO-d_6 as solvent. Purification of all compounds was generally achieved by recrystallization. The purity of compounds was generally ascertained by thin layer chromatography.

DFT calculations were performed on an HP workstation XW8600 with Xeon processor @ 2.8 GHz, 4 GB RAM and Windows Vista as operating system. The software package used was Gaussian 03 W [38] with Gauss View 4 as graphical program [39]. The ground state geometry was optimized at B3LYP functional and 6–31 G (d) as basis set. All the geometry optimizations were confirmed to be true by frequency analysis and showed no imaginary frequencies. Excited state calculations were performed by TD-DFT with B3LYP hybrid functional and 6–31 G (d) basis set.

Results and Discussions

The synthetic scheme for the synthesis of azoles is described in Fig. 1, 3-hydroxy-2-naphthalenecarboxylic acid (BON acid) was condensed with 2-aminothiophenol in toluene in the presence of PCl_3 as catalyst to obtain benzothiazole **3 (Step 1)** [35]. The azo dye **6 (Step 2)** [36] was prepared by reacting diazotized sulfanilic acid **4** and coupling with compound **3** under alkaline condition. The dye **6** was reduced at pH 7-8 by using sodium dithionite to obtain o-aminohydroxybenzothiazole **7 (Step 3)** [37]. Sulfanilic acid remains in the solution as sodium sulfanilate while the amine was suspended in the solution and filtered off. The cake was washed thoroughly with water to remove the sulfanilic acid. Compound **7** was then condensed with 2-hydroxybenzoic acid **8a** and 2, 4-dihydroxybenzoic acid **8b** to yield oxazoles **9a** and **9b (Step 4)**. Physical characteristics of compounds **7**, **9a** and **9b** are given in Table 1.

In these molecules –OH group at ortho to azole ring is acidic as compare to –N = of oxazole ring which is strongly basic. Under UV excitation, these two groups become strongly acidic and basic respectively. In excited state, proton is transferred from –OH group to hetero atom i.e. nitrogen to generate keto form. Hence ESIPT process occurred in these molecules. Mechanism of ESIPT occurred in molecule **9a** is given in Fig. 2.

Study of Photo Physical Properties

The absorption and emission of molecular species are influenced by the environment. The solvents used in making solutions of these molecular species provide a varied environment due to differences in dielectric constants and refractive indices of the solvents [14–17]. The ESIPT molecules **7**, **9a** and **9b** reported here are likely to exist in different conformational states. The conformer E* (Fig. 2) which forms hydrogen bonding with hetero atom (nitrogen) or with the polar solvents gives fluorescence.

Due to ESIPT phenomenon, oxazole derivatives of benzothiazole **9a** and **9b** showed single absorption having dual emission in less polar solvents. But these compounds showed three fluorescence emissions in polar aprotic solvent like DMF. This third emission peak observed is due to rotamer of enol form which may stabilise in DMF (Fig. 2). Due to ESIPT, these molecules show large Stokes shift (Table 1).

The effect of solvents (either as a pure solvent, such as ethanol, DMF, DMSO or as a mixture of solvents, such as different proportions of ethanol: water and DMF: ethanol) were studied in terms of absorption and fluorescence emission of the molecules (Table 2). In case of ethanol: water proportions, compounds are soluble minimum in 50 % of ethanol in water and as concentration of ethanol increases absorbance of compounds also increases. In case of ethanol: DMF proportions, there is no any significant change observed in absorbance (Table 2).

It is observed that these compounds show two fluorescence emission bands in less polar solvent like ethanol, but

Table 1 Physical characteristics of compounds

No.	Mol. Formula	Mol. weight	% Yield	Melting point (°C)	λ_{max} (nm) in DMF	Molar extinction coefficient (ε) (dm^3mol^{-1} cm^{-1}) in DMF	Fluorescence emission (nm) in DMF	Stokes shift (nm)	Relative quantum yield
7	$C_{17}H_{12}N_2OS$	292	90	162–164	332	46,800	372 440 562	050 108 230	0.00137
9a	$C_{24}H_{14}N_2O_2S$	394	72	140–142	330	22,400	384 432 558	054 132 228	0.00205
9b	$C_{24}H_{14}N_2O_3S$	410	69	170–172	322	22,600	356 454 528	034 132 206	0.00759

as polarity increases these compounds show three fluorescence emission bands. These compounds are found to be insoluble in non-polar solvents.

It has been found that as the polarity of the solvent increases, the intensity of third emission increases. DMF being more polar aprotic solvent gives the most intense emission. In the series of DMSO, DMF and ethanol, ethanol gives the least intense emission. When the polarity of DMF is decreased by adding ethanol, the fluorescence intensity of the third emission decreases progressively and finally diminishes in a 3:2 mixture of DMF: ethanol. Emission intensities of all three molecules in three pure solvents have been compared. It is seen that emission intensity increases with an increase in polarity, and in a highly polar aprotic solvent like DMF, three emissions are observed (Table 2).

Calculation of Relative Fluorescence Quantum Yield

Relative fluorescence quantum yield of compounds **7**, **9a** and **9b** are determined by using standards with known quantum yields (Fluorescein and Anthracene) and using **Formula 1** [40]. All these compounds are found to be dual emitting dyes

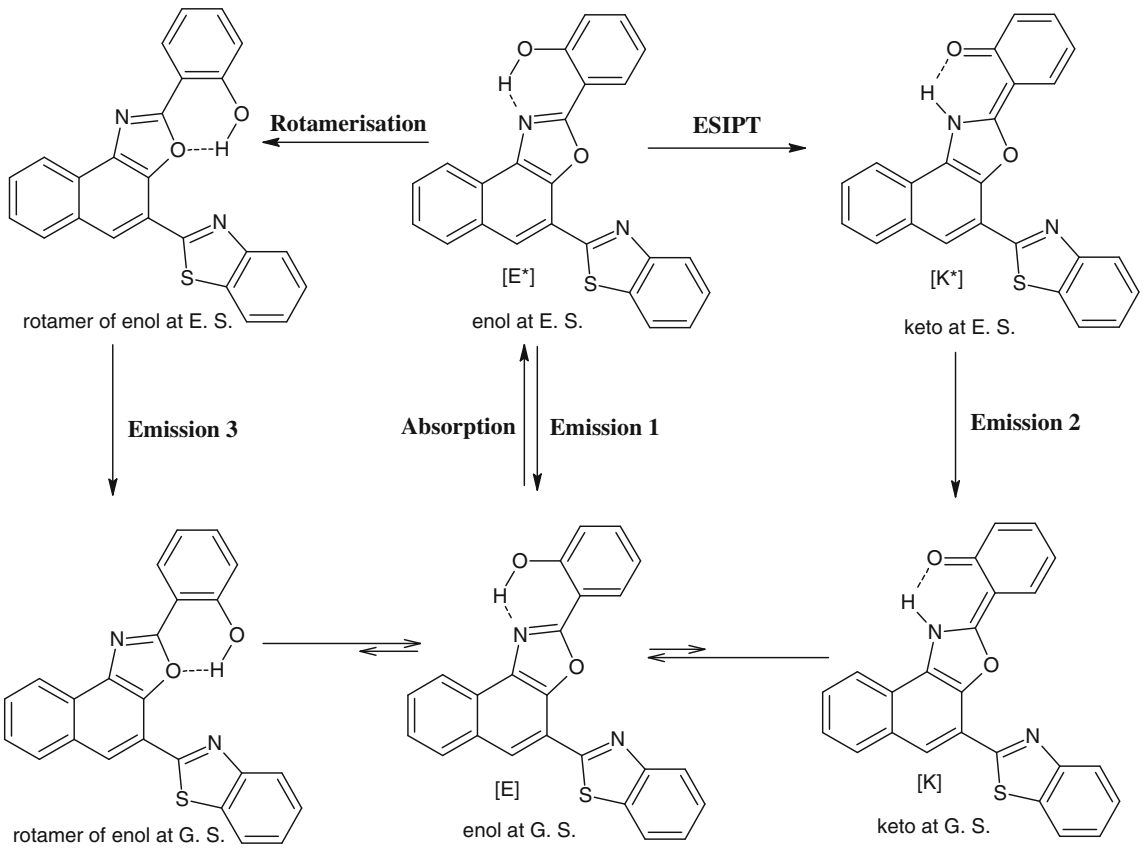

Fig. 2 Mechanism of ESIPT in molecule **9a**

Table 2 Effect of solvent polarity on photo-physical properties of compounds **7, 9a** and **9b**

Solvents	**7**		**9a**		**9b**	
	λ_{max}(nm), Absorbance (a.u.)	Emission wavelength (nm), Emission Intensity (a.u.)	λ_{max}(nm), Absorbance (a.u.)	Emission wavelength (nm), Emission Intensity (a.u.)	λ_{max}(nm), Absorbance (a.u.)	Emission wavelength (nm), Emission Intensity (a.u.)
50 % Ethanol: 50 % Water	330, 0.081	426, 0.037	330, 0.255	430, 0.114	330, 0.423	420, 0.083
		544, 0.025		536, 0.437		544, 0.080
60 % Ethanol: 40 % Water	330, 0.201	438, 0.015	330, 0.258	428, 0.110	330, 0.336	420, 0.072
		558, 0.043		534, 0.393		546, 0.071
70 % Ethanol: 30 % Water	330, 0.342	452, 0.021	330, 0.51	426, 0.065	330, 0.312	430, 0.134
		558, 0.086		552, 0.117		534, 0.421
80 % Ethanol: 20 % Water	330, 0.896	448, 0.029	330, 0.780	430, 0.071	330, 0.376	506, 0.114
		558, 0.133		552, 0.117		456, 0.101
90 % Ethanol: 10 % Water	330, 0.825	452, 0.062	330, 0.785	430, 0.081	330, 0.480	452, 0.360
		556, 0.112		552, 0.113		530, 0.360
100 % Ethanol	329, 1.101	438, 0.134	329, 0.919	438, 0.196	329, 0.492	452, 1.110
		550, 0.054		548, 0.084		524, 0.530
80 % Ethanol: 20 % DMF	330, 0.855	444, 0.139	330, 1.37	436, 0.165	318, 0.453	454, 0.625
		558, 0.104		554, 0.126		528, 0.494
60 % Ethanol: 40 % DMF	330, 0.742	452, 0.196	330, 0.761	438, 0.153	318, 0.630	456, 0.602
		560, 0.175		554, 0.126		530, 0.551
40 % Ethanol: 60 % DMF	330, 0.987	366, 1.668	330, 0.688	366, 1.904	321, 0.678	358, 1.753
		438, 1.884		430, 2.052		456, 4.553
		556, 1.367		554, 1.319		532, 4.260
20 % Ethanol: 80 % DMF	330, 0.698	364, 2.614	330, 0.918	366, 1.884	321, 0.512	354, 2.471
		434, 2.399		434, 2.403		454, 3.960
		544, 1.632		550, 2.058		530, 3.535
100 % DMF	332, 1.605	372, 1.139	330, 0.556	384, 3.101	322, 0.550	356, 2.795
		440, 2.512		432, 2.800		454, 4.033
		562, 1.327		558, 1.137		528, 3.291
100 % DMSO	330, 1.202	452, 0.541	330, 0.401	452, 0.510	330, 0.512	461, 0.819
		568, 1.017		566, 0.884		535, 0.866

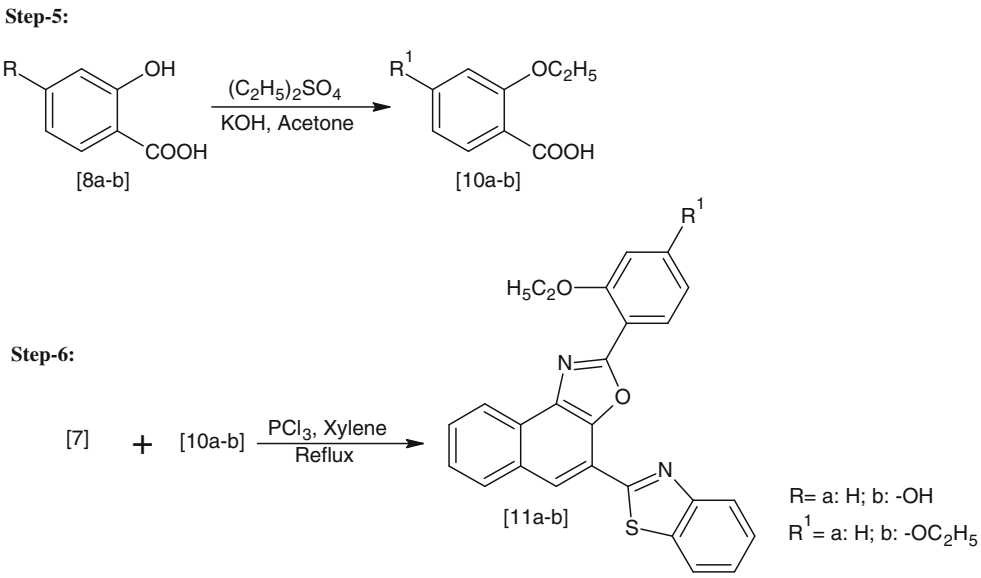

Fig. 3 Protection of –OH group

corresponding to their single excitation in less polar solvents. For compounds **7**, **9a** and **9b** two different quantum yields are reported at two different emissions. Quantum yields at long wavelength emission were calculated by using Fluorescein as a standard. Quantum yields at short wavelength emission were calculated using Anthracene as a standard. Solutions of different concentration (2 ppm to 10 ppm) in absolute ethanol for each sample were used for the measurement of absorbance and emission. Emission intensity values were plotted against absorption intensity values. These measurements gave a straight line graph, from which gradients were calculated for each compound and for standards. All the parameters such as solvent, cuvette and slit width were kept constant during the measurements to avoid errors**.** Relative fluorescence quantum yields of compounds **7**, **9a** and **9b** are mentioned in Table 1.

Formula 1: Relative Quantum Yield:

$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)$$

Where:

Φ_X	quantum yield of unknown sample
Φ_{ST}	quantum yield of standard used
$Grad_X$	gradient of unknown sample
$Grad_{ST}$	gradient of standard used
η_{ST}^2	refractive index of solvent for standard sample
η_X^2	refractive index of solvent for unknown sample

Confirmation for ESIPT Process

As we know phenolic –OH group plays an important role in ESIPT process. To confirm ESIPT, protection of this hydroxyl group was carried out using conventional method as shown in Fig. 3 and studied their photo physical properties.

Protection of –OH group:

Salicylic acid or Resorcylic acid (0.1 mol) was dissolved in acetone having (0.1 mol) KOH. Then added (0.12 mol) diethyl sulphate in it and reaction mass was stirred at room temperature. Reaction was monitored on TLC. Reaction was completed after 8 h. After this reaction mass was poured in

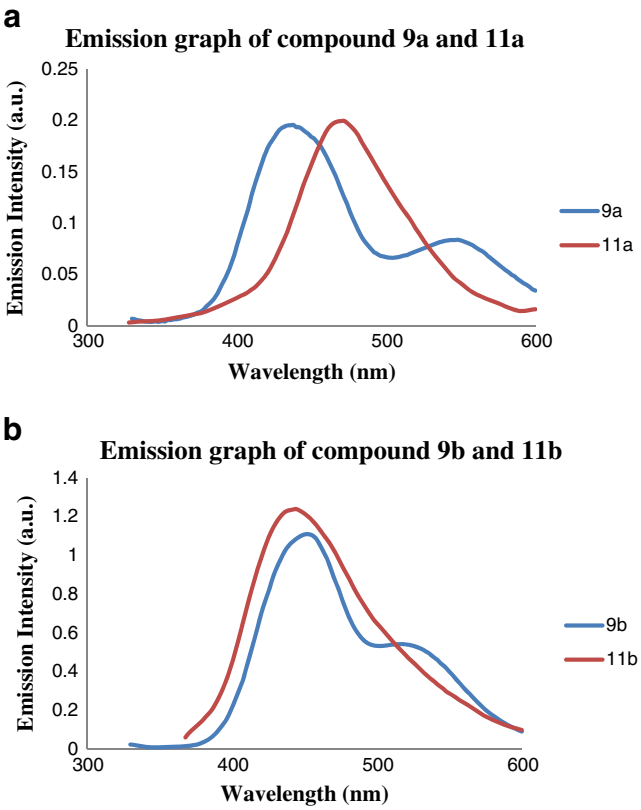

Fig. 4 ESIPT phenomenon confirmed by emission graph of protected and unprotected compounds. **a** Emission graph of compound **9a** and **11a** in ethanol. **b** Emission graph of compound **9b** and **11b** in ethanol

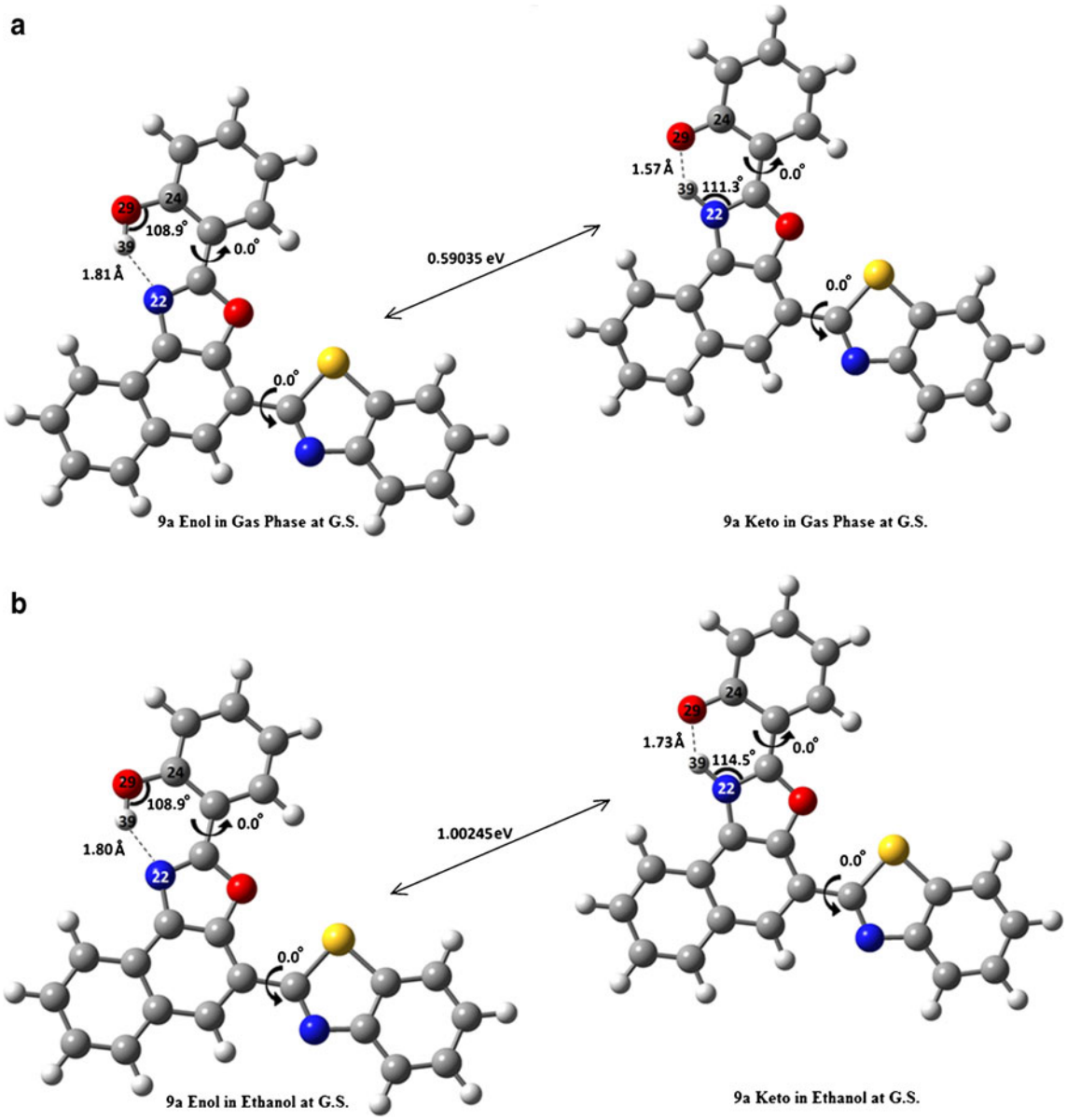

Fig. 5 **a** Optimized enol-keto structure of compound **9a** in gas phase at ground state. **b** Optimized enol-keto structure of compound **9a** in ethanol at ground state. **c** Optimized enol-keto structure of compound **9b** in gas phase at ground state. **d** Optimized enol-keto structure of compound **9b** in ethanol at ground state

water and extracted in ethyl acetate. Solvent was removed under reduce pressure to get **10a** and **10b**. These compounds **10a** and **10b** were cyclised with compound **7** using PCl_3 as a catalyst in xylene to give corresponding protected compounds **11a** and **11b** [35].

It was observed that ethylated products showed single absorption and single emission in ethanol as a solvent. Compound **11a** is having absorption at 328 nm and emission at 472 nm. Compound **11b** is having absorption at 345 nm and emission at 446 nm in ethanol.

Figure 4a and b indicate that protected hydroxyl group compounds i.e. **11a** and **11b** (o-ethylated) showed single emission as compare to ESIPT compounds **9a** and **9b**. In compounds **9a** and **9b** free hydroxyl group was taken part in ESIPT process to show single absorption having dual emissions. When this free hydroxyl was protected by ethyl group, there is no free proton available for tautomerization. Therefore these compounds showed single absorption with single emission. Longer wavelength emission band was disappeared in both protected molecules. ESIPT sequence gets destroyed in absence of proton at oxygen.

Density Functional Theory Calculations

The ESIPT phenomenon also can be explained on the basis of DFT calculations performed on compounds **9a** and **9b**. Using Gaussian 03 software package, optimization of

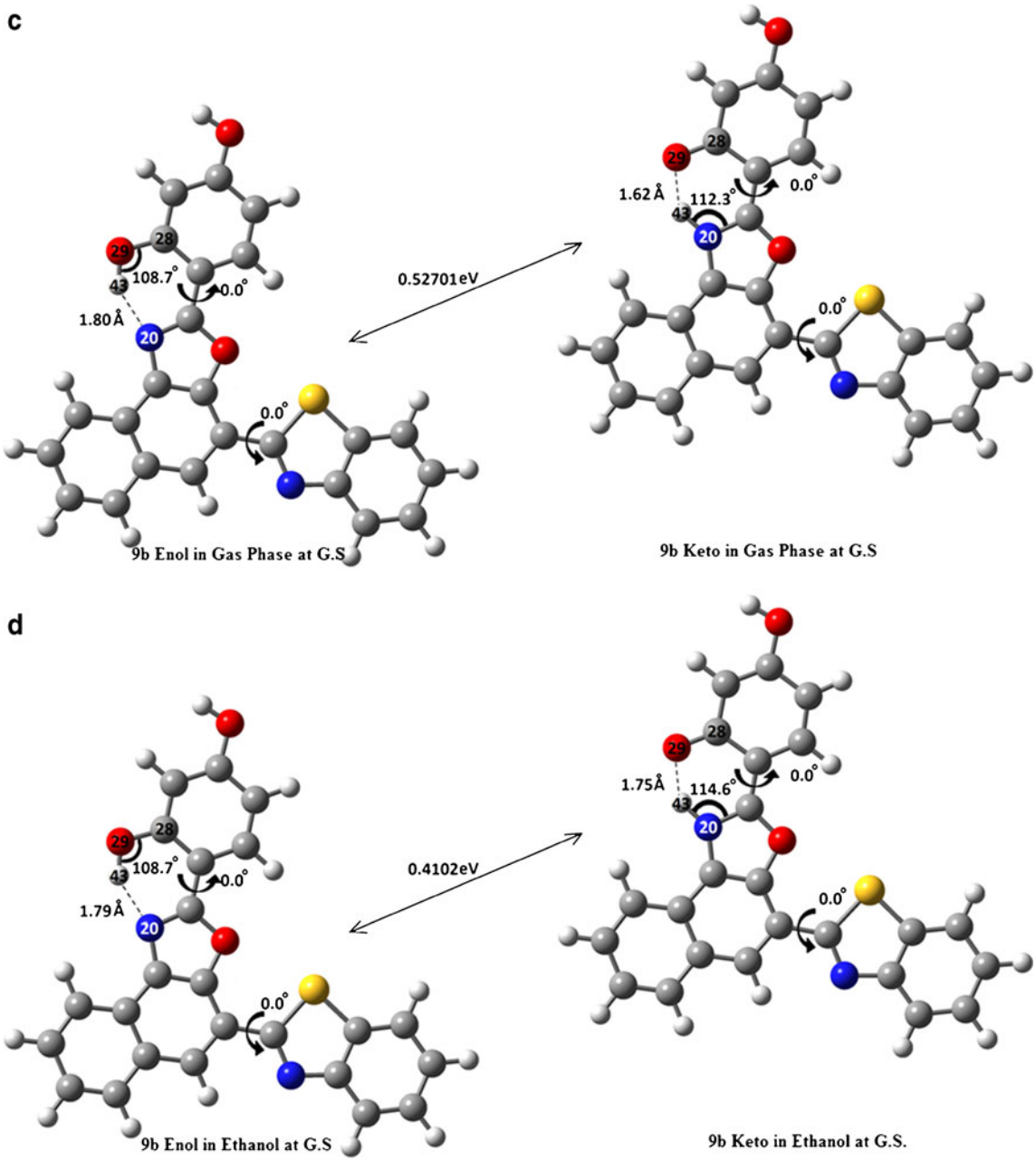

Fig. 5 (continued)

molecular enol- keto structures of compounds **9a** and **9b** at ground state in gas phase as well as in ethanol were carried out as shown in Fig. 5a, b, c, d respectively. Structural parameters like bond length, bond angle and dihedral

Table 3 Energy differences between enol-keto form and vertical excitations

	9a		**9b**	
	Gas phase	Ethanol	Gas phase	Ethanol
Vertical excitation E-E* (X)	3.6712 eV (337.72 nm)	3.6192 eV (342.57 nm)	3.7023 eV (334.88 nm)	3.6363 eV (340.96 nm)
Vertical excitation K-K* (Y)	3.4056 eV (364.06 nm)	3.5203 eV (352.20 nm)	3.3623 eV (368.74 nm)	3.4379 eV (360.64 nm)
Energy difference between enol-keto form in G. S. (Z eV)	0.59035 eV	1.00245 eV	0.52701 eV	0.4102 eV

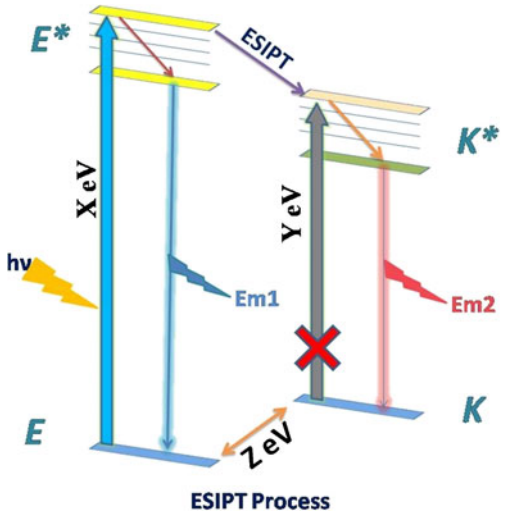

Fig. 6 Schematic representation of ESIPT process

angle of compounds **9a** and **9b** also have been shown in Fig. 5a, b, c, d.

Bond lengths of $\mathbf{C_{24}\text{-}O_{29}}$ in **9a** and that of $\mathbf{C_{28}\text{-}O_{29}}$ in **9b** in enol form are longer than double bonds and show a single bond character to respective C-O bonds of compounds **9a and 9b** respectively. The interatomic distances of $\mathbf{N_{22}\text{-}H_{39}}$ bond of compound **9a** and $\mathbf{N_{20}\text{-}H_{43}}$ bond of compound **9b** suggest a strong intramolecular hydrogen bonding between nitrogen from benzoxazole ring and hydrogen of hydroxyl group and favor the migration of proton from oxygen of hydroxyl group to nitrogen of oxazole ring. In case of compound **9b**, bond length of hydroxyl group (0.99109 °A) which participated in ESIPT process is more elongated than that of another hydroxyl group (0.97032 °A) present on same ring. It is also observed that the oxygen atom becomes more negative (−0.677 at excited state as compared to −0.673 at ground state) and makes the hydrogen more acidic for **9a**. Similarly in compound **9b** charge on oxygen becomes more negative (−0.702 at excited state as compared to −0.680 at ground state)

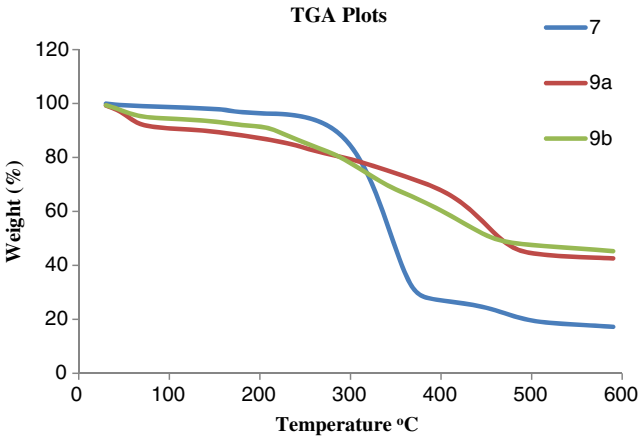

Fig. 7 Thermo gravimetric analysis

Table 4 Thermo gravimetric analysis of compounds **7**, **9a** and **9b**

Compound	TGA (°C)
7	260 (94 %)
9a	205 (86.93 %)
9b	200 (91.43 %)

and hydrogen becomes more positive. Dihedral angles between hydroxyl-phenyl ring and naphthoxazole, benzthiazole and naphthoxazole rings are almost zero which shows both the rings (thiazole and oxazole) are planar to naphthoxazole core. This facilitates ESIPT phenomenon.

These calculations have revealed that the ground state enol form of compound **9a** and **9b** are stabilized by 0.59035 eV (13.6158 Kcal/mole) and 0.52701 eV (12.1548 Kcal/mole) energy than its ground state keto form respectively (Table 3). And these are the only existing tautomers at ground state. Also practical observation of a single absorption peak supports this. Energy difference between vertical excitation E-E* is greater than the energy difference between vertical excitation K-K* in both gas phase and ethanol (Fig. 6). After undergoing ESIPT molecules **9a** and **9b** relax to lower vibronic states, and give emission with larger Stokes shift. The results of DFT calculation support the fact of dual emission due to ESIPT.

In the solvent DMF all molecules have shown triple emission. Though reason for this is not confirmed, this can be attributed to a stable intramolecular hydrogen bonded rotamer of enol (rotation of hydroxyl phenyl ring and H-bonding with oxygen) as which gets stabilized by polar aprotic solvent i.e. DMF.

Thermal Stability Study

Thermo gravimetric analysis of the molecules was carried out to study their thermal stability. The thermo gravimetric analysis (Fig. 7) shows that oxazoles derivatives have lower stabilities as compared with **7**. These results indicate that the dyes are stable up to 200 °C (Table 4).

Conclusion

The present work describes,

1. Simple synthesis and characterization of ESIPT molecules containing both oxazole and thiazole units.
2. The effect of polarity of solvents on ESIPT molecules and its role in the stabilization of different rotamers and tautomers in the ground state are studied.
3. Optimization of ESIPT molecules using Density Functional Theory was successfully carried out.
4. ESIPT phenomenon was confirmed by protection of phenolic –OH group which take part in ESIPT process.

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